ON THE GLASS TRANSITION TEMPERATURE

IN COVALENT GLASSES

by

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Abstract:

We give a simple demonstration of the formula relating the glass transition temperature, T_g, to the molar concentration x of a modifier in two types of glasses: binary glasses, whose composition can be denoted by $X_n Y_m + x\, M_p Y_q$, with X an element of III-rd or IV-th group (e.g. B, or Si, Ge), while $M_p Y_q$ is an alkali oxide or chalcogenide; next, the network glasses of the type $A_x B_{1-x}$, e.g. $Ge_x Se_{1-x}$, $Si_x Te_{1-x}$, etc. After comparison, this formula gives an exact expression of the parameter β of the modified Gibbs-Di Marzio equation.

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1   Introduction

The nature of glass transition is complex [1] and even today remains poorly understood. Numerous studies [2] have been devoted to measurements and understanding of the glass transition temperature, T_g, which is influenced by experimental conditions (e.g. the cooling rate of the melt). Nevertheless, even for the measurements under standard conditions, there is still no consensus as to which structural or thermodynamical factors are responsible for determining T_g. Kauzmann has observed that many glass-formers have $T_g \sim \frac{2}{3} T_{melting}$ [4]. Other attempts suggested correlation with molecular or atomic motions with characteristic energies that might be responsible for the observed values of T_g [5]. More recently, Tanaka discovered an empirical relationship between T_g and the average coordination number m per atom in glass : $ln\ T_g \sim 1.6m + 2.3$ [6].

Nevertheless, all these descriptions become more and more complicated if one starts to vary the composition x of glass forming material. Typical examples are the chalcogenide glasses (e.g. $As_x Se_{1-x}$) or binary glasses involving a network former (e.g. silica) and a modifier (an alkali oxide or chalcogenide, e.g. Li_2O). Some simple rules for predicting the glass transition temperature under standard conditions as function of the composition x and the nature of the atoms involved exist [3] among which Tanaka's relation [2], but there is still no general formulation of T_g versus x which could give the precise shape and explain with a mathematical model why maxima in glass transition temperature can occur (as in B_2O_3 based systems [7] or in $Ge_x Se_{1-x}$ glasses at x=0.33 [8]).

For many structural glasses, like the alkali-borate $(1 - x)\, B_2O_3 + x\, Li_2O$ glass, or the selenium-germanium network glass $Ge_x Se_{1-x}$, at least at low concentrations of the modifier, their glass transition temperature increases as even small amounts of modifier are added to the melt. In many cases the function, $T_g(x)$, is quasi-linear only for low modifier concentrations (small values of x), and in some cases (e.g. the aforementioned B_2O_3 and $Ge_x Se_{1-x}$ based glasses) displays a peak at some value of x, after which the derivative, $d\, T_g / d\, x$, changes its sign and becomes negative. An elegant explanation of this phenomenon, based on the evaluation of average number of constraints per structural unit, has been proposed for the $Ge_x Se_{1-x}$ alloy by J.C. Phillips ([9]).

We propose in this paper a simple and general model of glass formation

enabling us to derive the dependence of T_g on x, and a very simple formula for its derivative at $x = 0$. In the refs.[10] and [11] we have derived this formula and applied it to the particular case of alkali-borate glass; in this paper we show that it is confirmed by a large set of experimental data, concerning mainly network glasses.

It seems obvious that a liquid which is about to undergo the glass transition, during which its viscosity grows exponentially, is composed of many clusters, various in size and shape, agglomerating as the temperature decreases. Usually the process of solidification leading to the vitreous state, interpreted as a *continuous random network*, (the term introduced by Zachariasen, [12]) occurs in a small temperature range, (often a function of the cooling rate), between 30 and $40K$ around the average value called the *glass transition temperature* T_g [13]. It is known that the process is not a regular second order phase transition in the thermodynamical sense [14].

The most important elementary process of agglomeration, which is the creation of a new bond (usually an oxygen, sulfur or selenium bridge) between two clusters, can be analyzed in the ease of binary glasses. The modifier transforms the atoms of the glass former in a well defined manner (which may change when the concentration of the modifier increases); e.g., when a small amount of Li_2O is added to B_2O_3 glass, the ions of lithium transform the threefold boron atoms of the network former into fourfold boron atoms [7]; when the concentration x attains about 35%, the action of the modifier changes, and new lithium ions begin to depolymerize the network (by creating non-bridging oxygens), transforming the threefold boron atoms so that they have only 2 free bonds left that can participate in network formation. A similar modification of the atoms of glass former occurs in many other glasses; almost always, it amounts to the change of the coordination number of the elementary basic structure unit of the glass former (e.g. four-, three-, two-, one- and zero-fold tetrahedra in $IV - VI$ based glasses as $SiS_2 - Li_2S$ systems, corresponding to $SiS_4^{n\ominus}$ [n=4..0] units [15]).

2 The model

When the modifier's concentration is not too high, we assume that the probability of finding an "altered" atom with coordination number m' (such as a germanium atom in Ge_xSe_{1-x} systems) on the rim of an average cluster

is equal to x, and probability of finding a "regular" atom with coordination number m is $1 - x$ (such as a selenium atom in Ge_xSe_{1-x}). Let us denote the non-altered ("regular") atoms of the glass former by A, and the modified ("altered") atoms by B.

Our aim is to evaluate the time dependence of the fluctuations of local concentration (i.e. local variations of the variable x), and derive the equations imposing the minimization of these fluctuations. This minimum should then correspond to a stable or meta-stable configuration [16, 17]. With only two types of atoms there are three elementary processes of single bond formation, A-A, A-B and B-B.

The probabilities of these processes are proportional to the products of the relative concentrations of the atoms involved, the statistical factors which may be regarded as the degeneracies of the corresponding energies, and are proportional to the products of the corresponding valencies, and the Boltzmann factors involving the energies of respective bond formation. If we look at the newly created pairs, their probabilities will be:

$$p_{AA1} = \frac{m^2}{Q} (1 - x)^2 e^{-\frac{E_1}{kT}} \tag{1}$$

$$p_{AB1} = \frac{2mm'}{Q} x(1 - x) e^{-\frac{E_2}{kT}} \tag{2}$$

$$p_{BB1} = \frac{m'^2}{Q} x^2 e^{-\frac{E_3}{kT}} \tag{3}$$

where Q is the normalizing factor given by

$$Q = m^2 (1 - x)^2 e^{-\frac{E_1}{kT}} + 2mm' x (1 - x) e^{-\frac{E_2}{kT}} + m'^2 x^2 e^{-\frac{E_3}{kT}} \tag{4}$$

For the moment, we exclude the possibility of a simultaneous creation of two bonds leading to the formation of four- and six-membered rings; such posibility does exist in several glasses, and can be taken into account; then the number of elementary processes is bigger, but the analysis remains exactly the same [12, 13]. Anyhow, the network glasses we are considering here do not possess such an ability. Although the overall averages remain the same, the new pairs may create a local fluctuation in the statistics, which can be evaluated as:

$$x^{(1)} = \frac{1}{2} (2 p_{BB1} + p_{AB1}) \tag{5}$$

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Denoting the average time needed to form a new bond by τ, we can approximate the time derivative of x due to the above fluctuation as

$$\frac{d\,x}{d\,t} \simeq \frac{1}{\tau}\left[x^{(1)} - x\right] \tag{6}$$

which may be considered a good approximation as long as the time variation of the temperature, dT/dt, can be neglected, which is true when the quenching rate, $q = dT/dt$, satisfies:

$$\frac{1}{T}\frac{d\,T}{d\,t} = \frac{1}{T}q \ll \frac{1}{\tau} \tag{7}$$

This inequality is particularly well satisfied for the systems with which we shall be dealing. For example, borate and silicate based glasses form very easily, and have critical cooling rates of the order of $q_{crit} \simeq 10^{-4}K\,.s^{-1}$ [18]; so do other network glasses we are going to investigate [19].

Now, if we want to *minimize* the local fluctuations, we should equate the above expression to 0, which amounts to finding the *stationary* or *singular* solutions of the differential equation (6) This leads to:

$$\frac{d\,x}{d\,t} \simeq \frac{1}{\tau}\left(p_{BB1} + \frac{1}{2}p_{AB1} - x\right) = 0 \tag{8}$$

which leads to a simpler condition:

$$x(1-x)\left[m\,(1-x)\,(m'\,e^{-\frac{E_2}{kT}} - m\,e^{-\frac{E_1}{kT}}) + m'\,x\,(m'\,e^{-\frac{E_3}{kT}} - m\,e^{-\frac{E_2}{kT}})\right] = 0, \tag{9}$$

There are always two singular solutions at the points $x = 0$ and $x = 1$; there can exist also a third solution, given by the following expression:

$$x_{am} = \frac{mm'\,e^{-\frac{E_2}{kT}} - m^2\,e^{-\frac{E_1}{kT}}}{2\,mm'\,e^{-\frac{E_2}{kT}} - m'^2\,e^{-\frac{E_3}{kT}} - m^2\,e^{-\frac{E_1}{kT}}} \tag{10}$$

However, recalling that the variable x represents the modifier concentration, it is physically acceptable only if $0 \leq x_{am} \leq 1$; moreover, we want it to be an *attractive point,* which is possible only if:

$$\frac{m'}{m} > e^{\frac{E_2 - E_1}{kT}} \quad \text{and} \quad \frac{m}{m'} > e^{\frac{E_2 - E_3}{kT}}, \tag{11}$$

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We interpret the presence of the stable solution, x_{am}, as the manifestation of tendency of the system to become amorphous. On the contrary, when condition (11) is not satisfied, the stable (*attractive*) solution is found at $x = 0$, which means that at the microscopic level the agglomeration tends to separate the two kinds of atoms, A and B.

Note that due to the homogeneity of the expression (10), only *two* energy differences are essential here: $\alpha_1 = (E_2 - E_1)/kT$, and $\alpha_2 = (E_2 - E_3)/kT$.

Various glass formers display the tendency towards the solution x_{am} in a wide range of modifier concentration, also when it tends to zero ($x \to 0$). In this limit we get one condition only, which concerns only the energy difference $E_2 - E_1$:

$$E_2 - E_1 = k\,T_0\,ln(\frac{m'}{m}). \tag{12}$$

where T_0 is the glass transition temperature at $x = 0$, i.e. in the limit when the modifier concentration goes to zero.

This equation summarizes the relation between the *entropic* and *energetic* factors that are crucial for the glass forming tendency to appear. It tells us that in good binary glass formers whenever $m' > m$ (and $ln(\frac{m'}{m}) > 0$), one must have $E_2 > E_1$, and vice versa.

This condition is what should be intuitively expected indeed when a system displays the tendency towards amorphisation: it behaves in a "frustrated" way in the sense that the two main contributions to the probabilities of forming bigger clusters act in the opposite directions. Whenever the modifier raises the coordination number ($m' > m$), thus creating more degeneracy of the given energies E_i (i.e. much more possiblities of linking two entities A and B) and increasing the probability of agglomeration, the corresponding Boltzmann factor $e^{-\frac{E_2}{kT}}$ is smaller than for the non-modified atoms, $e^{-\frac{E_1}{kT}}$, reducing the probability of agglomeration, and vice versa.

Recalling that the stable solution corresponding to the glass-forming tendency defines an implicit function, $T(x)$, via the relation

$$m\,(1-x)\,(m'\,e^{-\frac{E_2}{kT}} - m\,e^{-\frac{E_1}{kT}}) + m'\,x\,(m'\,e^{-\frac{E_3}{kT}} - m\,e^{-\frac{E_2}{kT}}) \; = \; \Phi(x,T) = 0, \tag{13}$$

we can easily evaluate the derivative of T with respect to x:

$$\frac{dT}{dx} = -\left[\left(\frac{\partial\Phi}{\partial x}\right)/\left(\frac{\partial\Phi}{\partial T}\right)\right]_{\Phi(x,T)=0} \tag{14}$$

with m and m' representing the average number of free valencies of the two species of involved atoms.

In the limit $x = 0$ the result has a particularly simple form:

$$\left[\frac{dT}{dx}\right]_{x=0} = \left[\frac{d\,x_{am}}{d\,T}\right]_{T=T_0}^{-1} = \left[\frac{(2\,(m'/m)\,e^{\frac{E_1-E_2}{kT}} - 1)^2}{\frac{E_2-E_1}{kT^2}}\right]_{T=T_0} \tag{15}$$

Inserting condition (12), we obtain a general relation which can be interpreted as a universal law:

$$\left[\frac{dT}{dx}\right]_{x=0} = \frac{T_0}{ln(\frac{m'}{m})} \tag{16}$$

The glass transition temperature T_g in binary glasses increases with the addition of a modifier that increases the average coordination number $(m' > m)$, and decreases with the addition of a modifier that decreases the average coordination number $(m' < m)$.

3 Discussion

The formula (16) can be quite easily compared with experimental data. In Reference [11], we have demonstrated a good agreement of this formula with the behavior of dT_g/dx at $x = 0$ for the alkali-borate glass $(1-x)\,B_2O_3\,x\,Li_2O$ and the silicate glass $(1-x)\,SiO_2 + x\,CaO$. Formula (13) predicted $m'/m \simeq 3/2$ in the first case, which leads to a positive derivative, and $m'/m \simeq 1/3$ giving a negative one in the second case.

We have tried to find, whenever possible, reported glass transition temperatures of glass-forming systems which were composed of a very high fraction of "regular" atoms (e.g. selenium, sulphur or tellurium in the case of chalcogenide glasses), i.e. close to 95%, in order to approach the limit value $x \to 0$ of formula (16). We have applied this model to simple glass forming systems, namely chalcogenide based glasses, for which numerous experimental data are available. Within the ranges (close to $x = 0$) found in various references (see Table I and II), our formula agrees very well with the experimental data for the selenium based glasses (Table I). By "agreement", we mean the fact that the computation of the slope of T_g at $x = 0$ obtained with the experimental measured values, leads to very satisfying values of m'/m. Starting from pure vitreous selenium whose average glass transition temperature is $316\,K$

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(obtained by extrapolation from different experimental measurements [14]), we observe that all the considered glasses display an increase of the glass transition temperature with increasing x . Indeed, the *two valenced* selenium atoms form a network of chains with various length [20], hence $m = 2$ in this case. The atoms of the modifier (Ge, Si, As) produce cross-linking between the Se-chains, thus creating new stable structural units whose m' is equal to 4 (Si, Ge) or 3 (As) [21]. Obviously, equation (16) agrees only for the chalcogen-rich region, in particular for germanium selenide glasses. A similar phenomenon is observed in the Te- and S-based glasses. The average value of T_g of vitreous tellurium, obtained by averaging and extrapolation, is about $343\,K$ [6], whereas the T_g of pure vitreous sulphur is about $245\,K$ [14].

The tables below show a satisfactory agreement with our formula, and prove beyond any doubt that it is not a matter of coincidence.

Compound	$\left(\frac{m'}{m}\right)_{th}$	$\left(\frac{m'}{m}\right)_{exp}$	Obtained with		$\Delta T_g[K]$	Reference
			x	$T_g[K]$		
Ge_xSe_{1-x}	2.0	2.04	0.05	336	22	[8]
Si_xSe_{1-x}	2.0	2.04	0.05	336	22	[22]
As_xSe_{1-x}	1.5	1.54	0.003	318	2	[23]
Sb_xSe_{1-x}	1.5	1.31	0.15	493	177	[24]
P_xSe_{1-x}	2.5	2.53	0.05	333	17	[25]

Table I: *Different selenium based glasses. Comparison between the theoretical value of m'/m and the experimental value deduced from the slope using data of T_g for the lowest available concentration x.*

Compound	$\left(\frac{m'}{m}\right)_{th}$	$\left(\frac{m'}{m}\right)_{exp}$	Obtained with		$\Delta T_g[K]$	Reference
			x	$T_g[K]$		
Si_xTe_{1-x}	2.0	2.11	0.10	389	46	[26]
Ge_xTe_{1-x}	2.0	1.97	0.15	419	76	[27]
Ga_xTe_{1-x}	1.5	1.45	0.20	528	185	[28]
As_xS_{1-x}	1.5	1.54	0.11	307	63	[29]
Ge_xS_{1-x}	2.0	1.72	0.10	290	45	[30]

Table II: Different tellurium and sulphur based glasses. Comparison between the theoretical value of m'/m and the experimental value of m'/m deduced from the slope using data of T_g for the lowest available concentration x.

Nevertheless, we should mention that in certain glasses the equation (16) does not seem to be well satified. We believe that this problem is mostly due to the fact that certain modifiers exhibit already a metallic character; this may explain why our formula can not be applied to e.g. $Al_x Te_{1-x}$ glasses [31]. The covalent bonding with well-defined valencies is not well suited for the description of the network in this case.

A different type of problem arises in the systems which do not form glass below certain minimal value of x; it is obvious that our formula does not apply when glass can not be formed in the limit $x = 0$. Nevertheless, the formula can sometimes be extrapolated down to $x = 0$, when the variation of T_g versus x represents a straight line for greater values of x. The constant slope allows then a comparison with (16). In order to test the universality of the relation (16), experimental measurements in the very low x concentration range remain still to be realized (as for $As_x Se_{1-x}$, Table I) and also on the compounds which to our knowledge have never been investigated, such as $B_{.05} Se_{.95}$ and for which we predict $T_g \sim 355K$, and $B_{.05} S_{.95}$ for which we predict $T_g \sim 275K$.

4   Relationship with the Gibbs-Di Marzio equation

At the beginning of this article, we have mentioned that empirical relationships between glass transition temperature and several structural or physical properties have been proposed during the past ten years [3], [6]. Among these, we would like to focus our attention on the relation of equation (16) with the so-called "*Gibbs-Di Marzio*" equation which is particularly well adapted for predicting T_g in chalcogenide glasses. As described above (see figure 3), one can consider the chalcogenide glass system as a network of chains (e.g. selenium atoms) in which cross-linking units (such as germanium atoms) are inserted. Gibbs and Di Marzio [32] have developed a theory, based on

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equilibrium principles and assuming that glass transition is a second-order phase transition, which relates the increase of T_g to the growing presence of these cross-linking agents. They have applied successfully their theory to explain the T_g data in polymers [33, 34]. An adapted theory constructed by Di Marzio [35] has shown that for glass systems with some chain stiffness, the glass transition temperature versus cross-linking density X could be expressed as:

$$T_g = \frac{T_0}{1 - \kappa X} \tag{17}$$

where T_0 is the glass transition temperature of the initial polymeric chain and κ a constant.

Later on, Sreeram and co-workers [3] have modified this equation and have expressed T_g in terms of the network average coordination number $< r >$ which is widely used for the description of network glasses since Phillips has introduced the concept of $< r >$ in his constraint theory [36]. These authors have redefined for multicomponent chalcogenide glasses the cross-linking density X as being equal to the average coordination number of the cross-linked chain less the coordination number of the initial chain, i.e.:

$$X = < r > - 2 \tag{18}$$

The Gibbs-Di Marzio equation may then be rewritten as:

$$T_g = \frac{T_0}{1 - \beta(< r > -2)} \tag{19}$$

where β is a system depending constant, related eventually to the bond interchange [37] (which is responsible for the system dependent structural relaxation), whereas it was suggested that the constant κ is universal [35]. Sreeram et al. fitted (least-squares fit) the constant β to their T_g measurements [3] and obtained the value between:

$$0.55 < \beta < 0.75 \tag{20}$$

depending on the considered system and the involved atoms.

Let us now try to relate the modified Gibbs-Di Marzio equation to formula (16) in the pure chalcogen limit $x = 0$, in order to give an analytical expression of β. According to Phillips [36], we have expressed the average

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coordination number $< r >$ in terms of the coordination number of the covalently bonded atoms given by the $8 - N$ rule (where N is the number of the outer shell electrons), i.e. our previously defined factors m and m':

$$< r > = m(1 - x) + m'x \tag{21}$$

The slope at the origin, where $x = 0$ (and $< r >= m$) is then:

$$\left[\frac{d\,T_g}{d < r >}\right]_{<r>=m} = \frac{T_0}{(m' - m)\,ln\frac{m'}{m}} \tag{22}$$

which corresponds to a constant slope and to the straight line with equation:

$$T_g = T_0\left[1 + \frac{1}{(m' - m)\,ln\frac{m'}{m}}(< r > -m)\right] \tag{23}$$

In the vicinity of the pure chalcogen region, the Gibbs-Di Marzio can be expressed as:

$$T_g \simeq T_0\left[1 + \beta\,(< r > -2)\right] \tag{24}$$

which leads by identifying the two latter equations to an analytical expression of the constant β, involving only the coordination number m' and m. In Ref. [3], Sreeram started their investigation of multicomponent chalcogenide systems from pure vitreous selenium, hence $m = 2$:

$$\frac{1}{\beta} = (m' - m)\,ln(\frac{m'}{m}) \tag{25}$$

System	β_{fit}	Correlation coefficient	Reference
Ge_xSe_{1-x}	0.74	0.993	[8]
Ge_xSe_{1-x}	0.72	0.988	[3]
Ge_xSe_{1-x}	0.65	0.993	[38]
Ge_xS_{1-x}	0.73	0.998	[30]
Si_xSe_{1-x}	0.81	0.997	[22]

Table III: Computed values of β obtained from a least-squares fit, for different binary glass systems, compared to the value $\beta = 0.72$ calculated from equation (25).

The value of β can now be computed for binary systems if the coordination number of the atoms are known, e.g. for chalcogenide based glasses, the possible values for β are 0.36 (for $m' = 5$), 2.47 (for $m' = 3$) and 0.72 (for $m' = 4$). The latter situation corresponds to the glass Ge_xSe_{1-x} and the agreement of $\beta = 1/2ln(2) = 0.72$ with the value obtained by a least-squares fit of the glass transition temperatures data versus $< r >$, is very good. Other IV-II systems behave very similarly, as seen in Table III.

5   Summary and conclusion

We have derived in this paper an analytical formula from the statistical consideration of the agglomeration of coordinated entities (which may be identified with atoms or valenced clusters), which gives the slope of the glass transition temperature in very poorly modified binary systems X_xY_{1-x} with $x \simeq 0$:

$$\left[\frac{dT}{dx}\right]_{x=0} = \frac{T_0}{ln(\frac{m'}{m})} \tag{26}$$

The comparison of this formula with previously computed relationships of T_g with the concentration x or the average coordination number $< r >$, leads to an exact value of the β parameter of the modified Gibbs-Di Marzio equation of glass transition temperature.

$$\frac{1}{\beta} = (m' - m) \, ln(\frac{m'}{m}) \tag{27}$$

The formula seems to agree with systems investigated elsewhere.

We believe that such an attempt should be generalized for every concentration in binary glasses, in order to explain by means of the involved coordination numbers of the characterisitic clusters, the extrema of T_g in different systems such as Ge_xSe_{1-x} or B_2O_3 based glasses. Other direction of investigation should be the derivation of a similar formula for pseudo-binary or ternary glass systems, for which there is even more experimental data available. This work will be the subject of forthcoming papers.

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